



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: ELECTROLYTIC REACTOR SUCH AS FUEL CELL WITH ZEOLITE MEMBRANE			
(57) Abstract			
<p>An electrochemical reactor such as a fuel cell has a zeolite membrane (7) separating the anode (4) and cathode (5) compartments which allows the passage of ions through the membrane to carry an electric current, but prevents the passage of fuel molecules etc. through the membrane which might poison the catalyst used in the fuel cell. It is useful in methanol fuel cells using a basic electrolyte such as a carbonate salt and there can be a second zeolite membrane which prevents escape of methanol into the atmosphere which enables the fuel cell to operate at higher temperatures and hence be more efficient.</p>			
<div style="text-align: center;"> <math display="block">\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-</math> <math display="block">\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}</math> <p>Nett Reaction: <math>\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}</math></p> </div>			

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## ELECTROLYTIC REACTOR SUCH AS FUEL CELL WITH ZEOLITE MEMBRANE

The present invention relates to an improved electrolytic reactor.

Electrolytic reactors are reactors in which a chemical reaction is caused to take place by electrical means, for example a liquid compound or an ion in solution has one or more electrons added or removed from it to form a product, for example in the production of sodium hydroxide and chlorine from salt. Another major electrolytic process is the production of aluminium from bauxite.

There are a very large range of chemical processes, particularly electro-organic synthesis which theoretically can take place using an electrolytic reactor and such processes would have the advantage of taking place in solution, without the use of high temperatures and can often take place with high selectivity of the end product and with few, if any, side reactions.

In one type of electrolytic reactor there are separate cathode and anode compartments containing electrolyte. The cathode or anode can take an active part in the production of the desired end product, for example they can be in the form of a catalyst or they can be made from an electrical conducting material which is inert to the liquids with which it is in contact.

The anode and cathode compartments need to be separated to prevent diffusion of liquids between the compartments with consequent loss of performance, poisoning of electrodes etc. However an electric current must flow through the electrolyte and the production rate is a factor of the current flowing. This requirement of having an adequate current flowing through the electrolyte without there being the passage of liquid between the two compartments has been difficult to achieve in practice, and in spite of many proposals and the theoretical attractiveness of electrochemical reactions this has been one of the main reasons for the very limited applications of electrochemical processes.

A particular widely used application of an electrochemical reactor is a fuel cell.

In a typical fuel cell, each cell is divided by a membrane coated on both sides with a catalyst e.g. made of platinum and ruthenium. The anode compartment can hold a solution of the fuel in water, while the cathode compartment holds air as oxidising agent.

One problem of fuel cells using an organic fuel is that the fuel can diffuse from the anode compartment to the cathode compartment and can lead to a self discharge reaction in the cathode leading to lower cell voltage and efficiency. Cathodes which are inactive towards the oxidation of organic fuels can adsorb organic molecules on the cathode catalyst surface, which will lead to a lowering of their oxygen reduction efficiency.

Also organic fuel vapours are often harmful and their escape can lead to explosive mixtures being formed.

A well known type of fuel cell uses methanol as the fuel and liquid fuel cells have well tested advantages over hydrogen fuel cells. Other liquid fuels have been proposed and, in theory, any oxidisable liquid can be used as the fuel.

When methanol comes into contact with the catalyst, it breaks up to produce hydrogen ions, carbon dioxide and electrons. The flow of electrons out of the cell creates electricity. The hydrogen ions migrate across the membrane to the other side of the cell, combining with oxygen from the air to form water. Water and CO<sub>2</sub> are the cell's only waste products. However, with existing membranes, liquid methanol and methanol vapour can diffuse through the membrane and the crossover of methanol and methanol vapour from the anode to the cathode compartment can poison existing cathodes and reduce the cell voltage with loss of efficiency. Hence a need exists for a membrane which is impermeable to methanol but is permeable to hydrogen ions and to water. To date use has been made of membranes based on a fluorinated membrane made by Du Pont and sold under the Trade Name "Nafion". This basically consists of tetrafluorethylene with perfluorovinyl monomers having sulphonate functional groups allowing for the conduction of protons to provide the functional groups. This expensive leaky membrane is acknowledged as the weakest part of the cell design.

Other membranes with lower permeability to methanol and methanol vapour have been developed such as a polybenzimidazole or polyimidazole but these have lower ionic conductivity.

We have now devised an electrolytic reactor cell using a different type of membrane which reduces the problems of existing reactors.

According to the invention there is provided an electrolytic reactor comprising an anode compartment and a cathode compartment separated by a zeolite membrane and in which the anode compartment is adapted to contain a first compound in fluid form and the cathode compartment is adapted to contain a second compound in fluid form and in which an electric current can flow through the first and second compounds and the first and/or second compounds are chemically changed by the passage of the electric current.

In the case of a fuel cell the anode compartment contains an oxidisable fuel and the cathode compartment is adapted to contain air or other oxidising agent, there being a catalyst able to catalyse the oxidation of the fuel. The electrolyte in the fuel cell can be acidic or basic, when the electrolyte is acidic the zeolite membrane should be substantially resistant to acids and when the electrolyte is basic the membrane should be substantially resistant to alkalis. The cathode can comprise the catalyst which can be, for example a platinum or platinum group metal complex.

The zeolite membrane can be substantially impervious to acids by being formed from substantially acid resistant zeolites, e.g. zeolites and zeo-type materials which contain little or no aluminium or the zeolite membrane can be treated to render its surface substantially acid resistant.

Typical zeolites which can be used in the present invention include but are not limited to zeolites 3A, 4A, 5A, 13X, X, Y, ZSM5, MPOs, SAPOs, Silicalite,  $\beta$ ,  $\theta$ ,  $\epsilon$  etc.

When the electrolyte is basic the zeolite membrane can be substantially impervious to alkalis by being formed from substantially basic resistant zeolites, e.g. zeolites and zeo-type materials which are resistant to alkalis at a pH 10 and above for long periods

at elevated temperatures. See D.W. Breck "Zeolite Molecular Sieves", 1974 page 276 e.g. zeolite P.

In basic fuel cells the electrolyte can be any known electrolyte such as an alkali metal salt or hydroxide, alkaline earth metal salt or rare earth metal salt, preferably carbonate salts are used as these are carbon dioxide rejecting. Suitable salts include sodium carbonate, sodium bicarbonate, and their mixtures, for example the electrolyte can be a buffered carbonate/bicarbonate solution. A typical pH is in the range of 10 to 11. The alkaline earth metal salts which can be used include caesium carbonate etc.

The fuel cells of the present invention can be of the type which use an organic fuel and liquid water or an organic fuel and water vapour. When water vapour and an organic fuel is used, the vapour can be generated in a heated container containing the fuel plus water vapour mixture and fed into the anode compartment of the fuel cell. This enables the fuel cell to operate at higher temperatures with corresponding increase in efficiency.

It is a feature of zeolite membranes that they will allow water molecules and water vapour to pass through their pores but will prevent the passage of larger molecules such as methanol, ethanol, formates e.g. sodium formate molecules, in the liquid and vapour phases. Zeolite membranes which are hydrophilic can also allow water molecules and water vapour to pass through the membrane and prevent the passage of organic molecules.

In order to increase the conductivity of the cell, the liquid path length between the cathode and the anode is preferably reduced and this can be accomplished, for example, by having the zeolite membrane in contact with the anode or cathode or the zeolite membrane can be in substantial contact with the anode and cathode, so that a "sandwich" is formed comprising anode/zeolite membrane/cathode with the electrolyte substantially contained within the pores of the zeolite membrane.

A separate zeo -type membrane can be used to prevent the escape of fuel vapour into the atmosphere e.g. from the anode compartment. The membrane must be permeable to the waste products generated e.g. carbon dioxide and water, and impermeable to the fuel. This is particularly advantageous with volatile fuels such as methanol and enables

such fuel cells to operate at higher temperatures such as 80-90°C, without harmful gases escaping to the air or the risk of explosive mixtures being formed.

As no fuel such as methanol etc. can diffuse through the zeolite membrane into the cathode compartment there will be no escape of fuel from the cathode compartment. Thus the use of zeolite membranes in fuel cells have technical advantages over the use of existing membranes. The zeolite membranes should be substantially crack free and should contain substantially no defects which will allow the passage of methanol molecules.

Suitable zeolite membranes are described in co-pending patent applications PCT/GB 95/02221, PCT/GB 97/00635, PCT/GB 97/00928 and suitable electrodes are described in US Patent 5,470,073.

The zeolite membranes are made by conventional gel methods as described in the above applications and their surface is treated with a silicic acid or other compound to remove defects.

Preferably in use the membrane is from 0.1µm to 100µm thick. The pore cavity of the zeolite membrane is large enough to permit the passage of water molecules (2.6Å) but small enough to block the passage of the fuel molecules (3.8Å). Although a commonly proposed fuel is methanol, other fuels can be used e.g. methanol, ethanol, formate esters such as ethyl formate, ethers such as methyl tertiary butyl ether and hydrocarbons and the pore size and/or the affinity for the electrolyte of the zeolite membrane can be adjusted accordingly to prevent passage of the fuel molecules.

The presence of electrolyte through the pores of the membrane allows for ionic conductivity through the membrane and optionally the membrane can be treated to make it more conductive.

The material from which the substantially acid resistant membrane can be made are preferably of low aluminium content, e.g. mordenite or chabazite or aluminium free zeo-type compounds such as silicalite, gallium phosphates, USY, EDY, FDY, VPI-5, LZ210 described in US Patent 4,711,770 and others or materials formed by selective de-alumination of aluminosilicates as described in US Patent 5,242,676, or by

enriching aluminosilicates with silicon as described in US Patents 5,503,02A and 4,610,856A and EP82211A and as also described in D. W. Breck "Zeolite Molecular Sieves" 1974 page 503.

A membrane which is not acid resistant can be treated, for example, by passivating its surface, e.g. by forming a layer of an acid inert material on its surface, e.g. a layer of silica, yttria, zirconia, carbon, platinum, chromium, gold, or other acid resistant media.

If the pores of the membrane are too large, they can be "shrunk" by treatment with a sulphonic acid, e.g. a vinyl sulphonic acid or by a silicic acid or TEOS.

The design of the fuel cells used in the present invention can be of any known design in which a membrane separates the anode and cathode compartments. The anodes and cathodes which can be used are any known anodes and cathodes. The invention relates to the replacement of the previously disclosed membrane with a zeolite membrane as described above. Preferred electrodes are described in Fuel cells Past Present and Future by A. Tseung ISBN 1861660677. Greenwich University Press 1998.

Another type of fuel cell is a rechargeable fuel cell based on the dehydrogenation of a compound at the anode with diffusion of the hydrogen through a membrane to the cathode where it is oxidised electrochemically. On the charging cycle the process is reversed; this is in effect a method of storing hydrogen. The process has been proposed using cyclohexane which is reduced to benzene, however the membrane which was tried was silver-palladium membrane which was expensive and rendered the process impractical.

By the use of a zeolite membrane the hydrogen can diffuse through the membrane without either cyclohexane or benzene diffusing through to the other compartment.

The invention also provides a rechargeable fuel cell which comprises an anode compartment and a cathode compartment separated by a zeolite membrane and in which the anode compartment is adapted to contain a first compound in fluid form which is able to be dehydrogenated at the anode to generate an electric current which dehydrogenation reaction can be reversed by passing a current through the cell in the opposite direction to reform the first compound.



The cathode can be an air electrode and, when the first compound is cyclohexane which is dehydrogenated to benzene, the zeolite membrane will prevent diffusion of the cyclohexane and benzene into the cathode compartment where they would poison the electrode, whilst still allowing the diffusion of hydrogen through the membrane.

Another reaction which can be carried out by the use of the electrochemical reactor of the invention is the reduction of carbon dioxide to formic acid and methanol, the use of the zeolite membrane prevents the organic compounds from diffusing through to the anode compartment and oxidising the anode.

The invention is illustrated in the accompanying diagrammatic drawing of fig. 1 which shows illustrates a fuel cell.

In the drawing an anode (1) and cathode (2) are in contact with the acid electrolyte solution (3). Methanol or other fuel is in the anode compartment (4). Air (oxygen) is fed to the cathode compartment (5). The acid solution (6) is contained within the pores of the membrane (7). There is a platinum/ruthenium/carbon catalyst at (8) and a platinum/carbon catalyst at (9).

For methanol the reactions shown in the drawing take place. The use of the zeolite membranes of the invention prevent the passage of methanol or methanol vapour to the cathode whilst allowing conduction through the membranes by a salt bridge through the membrane..

#### Example

In order to test the acid resistance and ionic conductivity of zeolitic membranes the apparatus of fig. 2 was set up this comprises two glass chambers (11) and (12) between which is a zeolite membrane (15) sealed in place by silicone sealant (6) so that there is a passage between the two chambers only through membrane (15). In compartment (11) is a platinum counter electrode (17) and in chamber (12) is Teflon (RTM) PT/C cathode (14) and the chambers can be filled with electrolyte.

#### Acid electrolyte

The apparatus was filled with 1 molar sulphuric acid at room temperature. The cathode gave 70 mA/cm<sup>2</sup> at 0.5V at 500mV vs RHE. There was no change in the

cathode performance over a test period of 3 hours when 0.5 molar methanol or 0.5M ethyl formate was added to chamber. When the membrane was removed the cathode performance decreased to 10 mA/cm<sup>2</sup>, indicating severe poisoning of oxygen reduction activity by methanol and ethyl formate.

#### Alkaline electrolyte

The test was repeated with a buffered Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> electrolyte. The membrane was prepared as in Example 3 of PCT/GB95/02221 and was 20 microns thick, the membrane was soaked in the electrolyte solution and its properties measured.

#### Results

#### 1. Properties of Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> electrolyte solution with the zeolite membrane soaked with the electrolyte solution.

##### 1.1 Conductivity of 0.5M Na<sub>2</sub>CO<sub>3</sub>/0.5MNaHCO<sub>3</sub>

Temperature °C	Conductivity ohm <sup>-1</sup> .cm <sup>-1</sup>
25	0.0824
40	0.1034
60	0.1312

##### 1.2 Resistivity of 0.5M Na<sub>2</sub>CO<sub>3</sub>/0.5MNaHCO<sub>3</sub>

Temperature °C	Resistivity ohm.-cm
25	12.1
40	9.7
60	7.6

##### 1.3 Resistance of zeolite membrane impregnated with 0.5M Na<sub>2</sub>CO<sub>3</sub>/0.5MNaHCO<sub>3</sub>

Temperature °C	Resistance ohm.
25	1.1
40	0.9
60	0.8

## 2. Half cell performance:-

### 2.1 Anode performance

Anode: Pt-Ru-WO<sub>3</sub>/C (1:0.5:1:7.5 W/W), Pt-Ru loading ~2mg.cm<sup>-2</sup>  
Solution: 0.5M Na<sub>2</sub>CO<sub>3</sub>/0.5MNaHCO<sub>3</sub> /1.0MCH<sub>3</sub>OH  
Performance: CH<sub>3</sub>OH oxidation, 0.25V vs RHE, 20mA.cm<sup>-2</sup> at 60°C

### 2.2 Cathode Performance

Cathode: Pt/C (0.5:9.5 W/W), Pt loading ~ 1mg.cm<sup>-2</sup>  
Solution: 0.5M Na<sub>2</sub>CO<sub>3</sub>/0.5MNaHCO<sub>3</sub>  
Performance: O<sub>2</sub> reduction, 0.7V vs RHE, 20mA.cm<sup>-2</sup> at 60°C

The anode was teflon bonded with a thin layer of Nafion dispersion and the distance of the Luggin tip to the working electrode was ~2mm.

The cathode was teflon bonded and with no zeolite membrane and in the absence of CH<sub>3</sub>OH gave 0.7 V 20mA cm<sup>-2</sup> in still air, 1MCH<sub>3</sub>OH was added and the performance dropped to 0.3V 20mA cm<sup>-2</sup> due to the poisoning of the of the oxygen reduction reaction and the short circuit current generation between the Pt and C sites for the oxidation of methanol.

When the zeolite membrane was placed between the anode and cathode compartments, the cathode performance remained constant regardless whether methanol was present in the anode compartment.

## 3. Full cell performance

The membrane was prepared by depositing the zeolite membrane onto the cathode and pasting the anode catalyst and nickel screen on the zeolite membrane surface, the full cell performance gave 0.25V at 20mA/cm<sup>2</sup> and the performance was stable over a test of 3 hours at 60°C.

The use of a zeolite membrane with a buffered Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> electrolyte gave adequate ionic conductivity, was CO<sub>2</sub> rejecting and there was no detectable corrosion of the membrane at test temperatures up to 60°C and test periods of up to a week.

Fig. 3 shows plot of current density on the air cathode against time with and without methanol in which:-

Pt/C 5%	(Working electrode)
SCE	(Reference electrode)
Pt black	25°C (Counter electrode)

Electrolyte Solution- 0.5M  $\text{Na}_2\text{CO}_3$ /0.5M  $\text{NaHCO}_3$

CA01 without  $\text{CH}_3\text{OH}$

CA31 1M  $\text{CH}_3\text{OH}$

As can be seen the cathode performance at 0.7v vs RHE shows that the use of membrane leads to no poisoning by methanol.

## Claims

1. An electrolytic reactor comprising an anode compartment and a cathode compartment separated by a zeolite membrane and in which the anode compartment is adapted to contain a first compound in fluid form and the cathode compartment is adapted to contain a second compound in fluid form and in which an electric current can flow through the first and second compounds and the first and/or second compounds are chemically changed by the passage of the electric current.
2. An electrolytic reactor as claimed in claim 1 in which the anode compartment is adapted to contain an oxidisable fuel and the cathode compartment is adapted to contain air or other oxidising agent, there being a catalyst able to catalyse the oxidation of the fuel.
3. An electrolytic reactor as claimed in claim 1 which comprises an anode compartment and a cathode compartment separated by a zeolite membrane and in which the anode compartment contains a first compound in fluid form and the cathode compartment contains a second compound in fluid form and in which there is an electrolyte in the anode and cathode compartments and in the pores of the zeolite membrane and in which an electric current can flow through the first and second compounds and the first and/or second compounds are chemically changed by the passage of the electric current.
4. An electrolytic reactor as claimed in claim 3 or 4 in which the anode compartment contains an oxidisable fuel and the cathode compartment contains air or other oxidising agent, there being a catalyst able to catalyse the oxidation of the fuel.
5. An electrolytic reactor as claimed in claim 3 in which the electrolyte is basic and the membrane is substantially resistant to alkalis.
6. An electrolytic reactor as claimed in claim 5 in which the electrolyte is an alkali metal salt or hydroxide, an alkaline earth metal salt or rare earth metal salt,
7. An electrolytic reactor as claimed in claim 5 in which the electrolyte is a carbonate salt.

8. An electrolytic reactor as claimed in claim 6 in which the electrolyte is sodium carbonate, sodium bicarbonate or a mixture of sodium carbonate and sodium bicarbonate.
9. An electrolytic reactor as claimed in claim 3 or 4 in which the electrolyte is acidic and the zeolite membrane is substantially resistant to acids.
10. An electrolytic reactor as claimed in claim 9 in which the zeolite membrane is treated to render its surface substantially acid resistant.
11. An electrolytic reactor as claimed in claim 9 in which the zeolite membrane is formed from substantially acid resistant zeolites and zeo-type materials which contain little or no aluminium.
12. An electrolytic reactor as claimed in any one of claims 2 and 4 to 11 in which the cathode comprises the catalyst.
13. An electrolytic reactor as claimed in claim 12 in which the catalyst is a platinum or platinum group metal complex.
14. An electrolytic reactor as claimed in any one of the preceding claims in which the zeolite membrane is in contact with the anode or cathodes.
15. An electrolytic reactor as claimed in any one of the preceding claims in which the zeolite membrane is in contact with the anode and cathode so that a sandwich is formed comprising anode/zeolite membrane/cathode with the electrolyte substantially contained within the pores of the zeolite membrane.
16. An electrolytic reactor as claimed in any one of the preceding claims which is a fuel cell in which the first compound is an organic fuel.
17. A fuel cell as claimed in claim 16 in which the first compound is an organic fuel and liquid water or an organic fuel and water vapour.

18. A fuel cell as claimed in claim 17 in which the first compound is an organic fuel and water vapour and water the vapour is generated in a heated container containing the fuel plus water vapour mixture and fed into the anode compartment of the fuel cell.

19. A fuel cell as claimed in any one of claims 16 to 18 in which the organic fuel is methanol, ethanol, a formate esters, an ether or a hydrocarbon and the pore size of the zeolite membrane prevent passage of the fuel molecules from the cathode to the anode compartments.

20. A fuel cell as claimed in any one of claims 16 to 19 in which there is a second zeolite membrane which prevents the escape of fuel vapour into the atmosphere.

21. A fuel cell as claimed in any claim 22 in which the second zeolite membrane is permeable to the waste products generated by the oxidisation of the fuel and impermeable to the fuel.

22. An electrolytic reactor as claimed in claim 3 or 4 which is a rechargeable fuel cell which comprises an anode compartment and a cathode compartment separated by a zeolite membrane and in which the anode compartment contains a first compound in fluid form which is able to be dehydrogenated at the anode to generate an electric current which dehydrogenation reaction can be reversed by passing a current through the cell in the opposite direction to reform the first compound.

23. An electrolytic reactor as claimed in claim 22 in which the cathode is an air electrode.

24. An electrolytic reactor as claimed in claim 22 or 23 in which the first compound is cyclohexane which is dehydrogenated to benzene and the zeolite membrane prevents diffusion of the cyclohexane and benzene into the cathode compartment whilst still allowing the diffusion of hydrogen through the membrane.

25. An electrolytic reactor as claimed in claim 3 or 4 which comprises an anode compartment and a cathode compartment separated by a zeolite membrane and in which the anode compartment contains a first compound in fluid form which is able to

be dehydrogenated at the anode and in which the first compound is carbon dioxide which is reduced to formic acid and methanol and the zeolite membrane prevents the organic compounds from diffusing through to the anode compartment and oxidising the anode.

26. An electrolytic reactor as claimed in any one of the preceding claims in which the zeolite membrane is from 0.1 $\mu$ m to 100 $\mu$ m thick.

27. An electrolytic reactor as claimed in any one of the preceding claims in which the pore cavity of the zeolite membrane is large enough to permit the passage of water molecules but small enough to block the passage of the fuel molecules.

28. An electrolytic reactor as claimed in any one of the preceding claims in which the pore cavity of the zeolite membrane is between (2.6Å) and (3.8Å).



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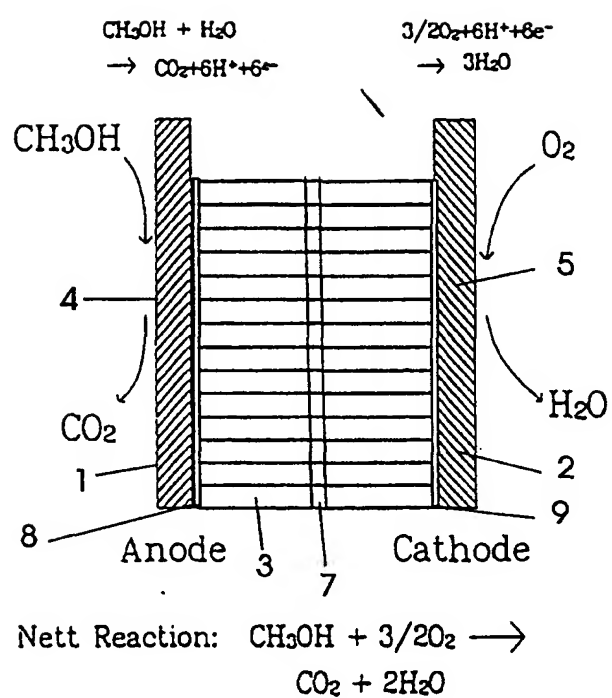


Fig. 1

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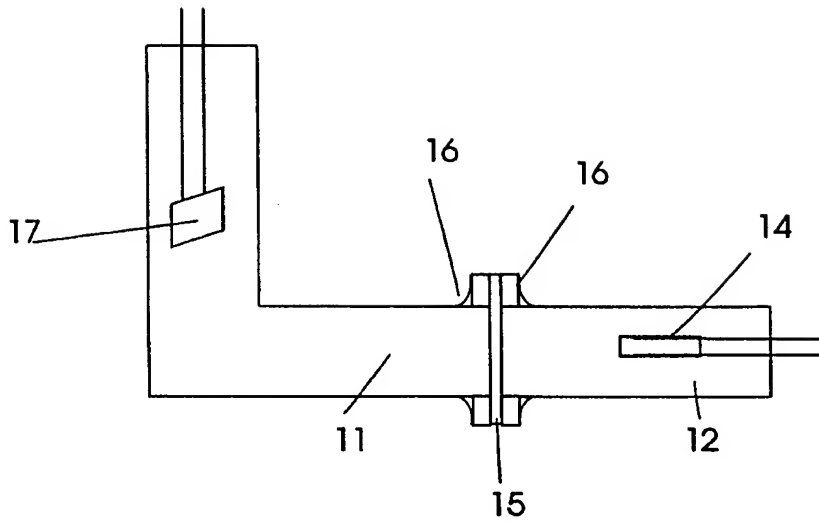


Fig. 2

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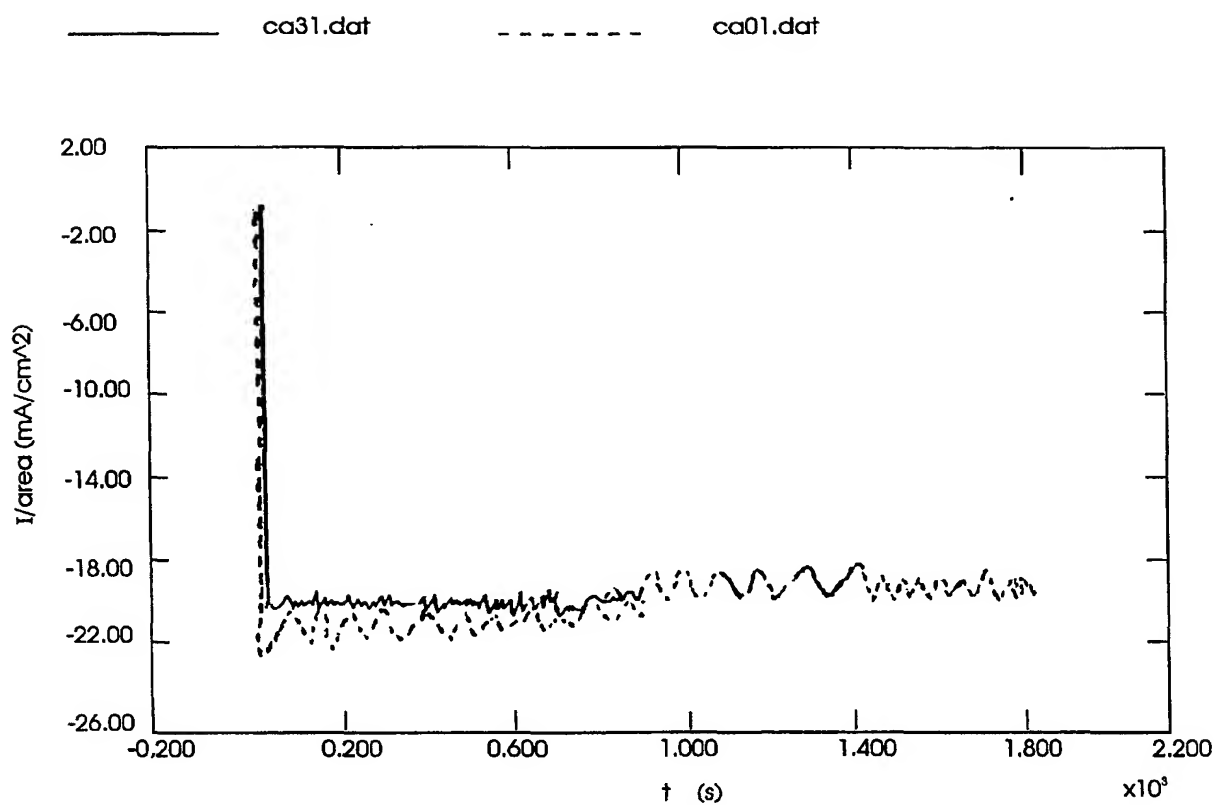


Fig. 3

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 98/01380

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6    H01M8/08    H01M8/10    H01M8/02    C25B5/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6    H01M    C25B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 266 940 A (PHILIP D. CAESAR) 16 August 1966  see column 3, line 61 - column 4, line 13; claims 1,2; figure 1 see column 2, line 68 - column 3, line 36 see column 1, line 31 - column 2, line 3	1,2,4-9, 12,15, 16,26
Y	---	13
Y	US 3 236 693 A (PHILIP D. CAESAR) 22 February 1966 see claims 1,5	13
X	US 3 421 948 A (ARRANCE FRANK C ET AL) 14 January 1969 see column 2, line 41 - column 3, line 21; claim 1; figure 1	1-4,9,12
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<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-weight: bold;">3 September 1998</div>		Date of mailing of the international search report  <div style="text-align: center; font-weight: bold;">24/09/1998</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-weight: bold;">D'hondt, J</div>

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01380

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X	<p>DATABASE WPI  Section Ch, Week 8337  Derwent Publications Ltd., London, GB;  Class E33, AN 83-762899  XP002076341  &amp; RO 81 348 A (INST POLITEHNIC ASACHI G)  see abstract  -&amp; CHEMICAL ABSTRACTS, vol. 100, no. 16,  16 April 1984  Columbus, Ohio, US;  abstract no. 123503,  CRUCEANU ET AL: "Zeolite molecular  sieves"  XP002076338  see abstract  &amp; RO 81 348 A (INSTUTUL POLITEHNIC  "GEORGHE ASACHI") 28 February 1983</p>	<p>1-6, 12,  16, 19</p>
Y	<p>---</p>	<p>1-4,  12-17, 19</p>
Y	<p>WO 96 29752 A (DU PONT ;GROT WALTHER  GUSTAV (US); RAJENDRAN GOVINDARAJULU (US))  26 September 1996  see claims 1, 2, 4, 6, 18, 19, 22  see page 9, line 33 - page 10, line 3  see page 14, line 20 - page 15, line 20;  example 2</p>	<p>1-4,  12-17, 19</p>
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P, Y	<p>---</p> <p>WO 97 19480 A (CALIFORNIA INST OF TECHN  ;YEN SHAO PING S (US); NARAYANAN SEKHARI)  29 May 1997  see page 25, line 1 - line 27; claims  34, 38, 40; figure 1</p> <p>---</p> <p>-/---</p>	<p>1-3,  12-17, 19</p>

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